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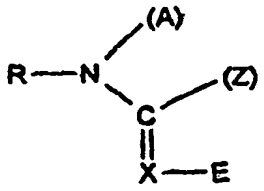
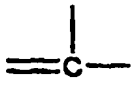
(54) Title: WOOD PRESERVATIVES FOR INCORPORATION INTO BINDERS

(57) Abstract

The application relates to mixtures of binders or adhesives which can be employed for the manufacture of plywood and timber materials with compounds of general formula (I) in which R represents hydrogen, optionally substituted radicals of the group consisting of acyl, alkyl, aryl, aralkyl, heteroaryl and heteroarylalkyl; A represents a monofunctional group from the series hydrogen, acyl, alkyl, aryl, or represents a bifunctional group which is linked to the radical Z; E represents an electron–withdrawal radical; X represents the radicals –CH= or =N–, it being possible for the radical –CH= to be linked to the radical Z instead of an H atom; Z represents a monofunctional group from the series alkyl, –O–R, –S–R, (a) or represents a bifunctional group which is linked to the radical A or the radical X; the compound Imidocloprid being particularly preferred.



(I)



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Wood preservatives for incorporation into binders

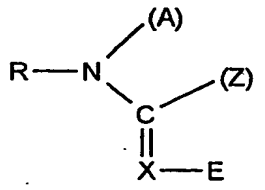
The application relates to wood preservatives which can be employed in the manufacture of plywood and timber materials.

Plywood and timber materials such as, for example, chipboards are in general treated with wood preservatives by two methods. Firstly, by treating the wood with wood preservatives before processing to give timber materials and secondly, by impregnating the surface of the finished timber materials, e.g. by pressure. Both processes in general lead to deformations and swellings in the sheet treated in this way. On the other hand, it is known that a process for the manufacture of plywood sheets would be most efficient if insecticides, termiticides and fungicides could be incorporated directly into the adhesives during sheet manufacture.

Using the wood preservatives known until now, however, this was not possible until now as these compositions decompose or evaporate under the process conditions necessary for the manufacture of the sheets.

The compositions according to the invention do not have these disadvantages.

The application therefore relates to mixtures of binders or adhesives which can be employed for the manufacture of plywood and timber materials with compounds of the general formula (I)



(I)

in which

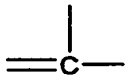
R represents hydrogen, optionally substituted radicals of the group consisting of acyl, alkyl, aryl, aralkyl, heteroaryl and heteroarylalkyl;

A represents a monofunctional group from the series hydrogen, acyl, alkyl, aryl, or represents a bifunctional group which is linked to the radical Z;

E represents an electron-withdrawal radical;

X represents the radicals -CH= or =N-, it being possible for the radical -CH= to be linked to the radical Z instead of an H atom;

Z represents a monofunctional group from the series alkyl, -O-R, -S-R,



or represents a bifunctional group which is linked to the radical A or the radical X.

Particularly preferred compounds of the formula (I) are those in which the radicals have the following meaning:

R represents hydrogen and optionally substituted radicals from the series acyl, alkyl, aryl, aralkyl, heteroaryl, heteroarylalkyl.

Acyl radicals which may be mentioned are formyl, alkylcarbonyl, arylcarbonyl, alkylsulphonyl, arylsulphonyl, (alkyl-)-(aryl-)-phosphoryl, which for their part can be substituted.

Alkyl which may be mentioned is C_{1-10}-alkyl, in particular C_{1-4}alkyl, specifically methyl, ethyl, i-propyl, sec- or t-butyl, which for their part can be substituted.

Aryl which may be mentioned is phenyl, naphthyl in particular phenyl.

Aralkyl which may be mentioned is phenylmethyl, phenethyl.

Heteroaryl, which may be mentioned is heteroaryl having up to 10 ring atoms and N, O, S, in particular N, as heteroatoms. Thienyl, furyl, thiazolyl, imidazolyl, pyridyl, benzothiazolyl may specifically be mentioned.

Heteroarylalkyl which may be mentioned is heteroarylmethyl, heteroarylethyl having up to 6 ring atoms and N, O, S, in particular N, as heteroatoms.

Substituents which may preferably be mentioned by way of example are: alkyl preferably having 1 to 4, in particular 1 or 2, carbon atoms, such as methyl, ethyl, n- and i-propyl and n-, i- and t-butyl; alkoxy preferably having 1 to 4, in particular 1 or 2 carbon atoms, such as methoxy, ethoxy, n- and i-propyloxy and n-, i- and t-butyloxy; alkylthio preferably having 1 to 4, in particular 1 or 2 carbon atoms, such as methylthio, ethylthio, n- and i-propylthio and n-, i- and t-butylthio; halogenoalkyl preferably having 1 to 4, in particular 1 to 2 carbon atoms and preferably 1 to 5, in particular 1 to 3 halogen atoms, the halogen atoms being identical or different and, as halogen atoms, are preferably fluorine, chlorine or bromine, in particular fluorine, such as trifluoromethyl; hydroxy; halogen, preferably fluorine, chlorine, bromine and iodine, in particular fluorine, chlorine and bromine; cyano; nitro; amino; monoalkyl- and dialkylamino preferably having 1 to 4, in particular 1 or 2 carbon atoms per alkyl group, such as methylamino, methyl-ethyl-amino, n- and i-propylamino and methyl-n-butylamino; carboxyl; carbalkoxy preferably having 2 to 4, in particular 2 or 3 carbon atoms, such as carbomethoxy and carboethoxy; sulpho ($-SO_3H$); alkylsulphonyl preferably having 1 to 4, in particular 1 or 2 carbon atoms, such as methylsulphonyl and ethylsulphonyl; arylsulphonyl preferably having 6 or 10 aryl carbon atoms, such as phenylsulphonyl, and heteroarylamino and heterarylalkylamino such as chloropyridylamino and chlorpyridylmethylamino.

A particularly represents hydrogen and optionally substituted radicals from the series acyl, alkyl, aryl, which preferably have meanings given in the case of R.

A furthermore represents a bifunctional group. Optionally substituted alkylene have 1-4, in particular 1-2, C atoms may be mentioned, whereas substituents the substituents listed further above may be mentioned and where the alkylene groups can be interrupted by heteroatoms from the series N, O, S.

A and Z, together with the atoms to which they are bonded, can form a saturated or unsaturated cyclic ring. The heterocyclic ring can contain a further 1 or 2 identical or different heteroatoms and/or heterogroups. Heteroatoms are preferably oxygen, sulphur or nitrogen and heterogroups are N-alkyl, alkyl of the N-alkyl group preferably containing 1 to 4, in particular 1 or 2 carbon atoms. Alkyl which may be mentioned is methyl, ethyl, n- and i-propyl and n-, i- and t-butyl. The heterocyclic ring contains 5 to 7, preferably 5 or 6, ring member.

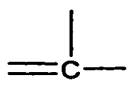
Examples of the heterocyclic ring which may be mentioned are imidazolidine, pyrrolidine, piperidine, piperazine, hexamethylenimine, hexahydro-1,3,5-triazine, hexahydrooxodiazine, morpholine, each of which, if appropriate, may preferably be substituted by methyl.

E represents an electronic-withdrawing radical, where in particular NO_2, CN, halogenalkylcarbonyl such as 1,5-halogeno-C_{1-4}-carbonyl, in particular $COCF_3$, may be mentioned.

X represents -CH= or -N=

Z represents optionally substituted radicals alkyl, -OR, -SR, -NRR, R and the substituents preferably having the meaning given above.

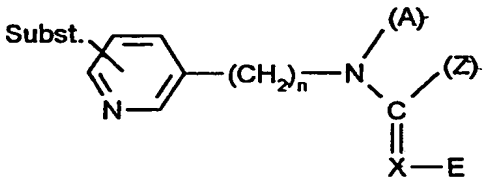
Z can additionally to the abovementioned ring, together with the atom to which it is bonded and the radical



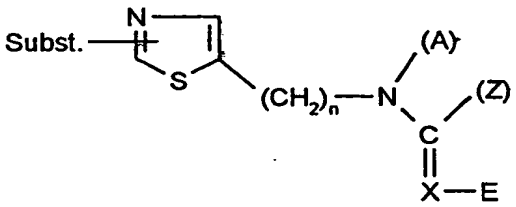
form a saturated or unsaturated heterocyclic ring in the position of X. The heterocyclic ring can contain a further one or two identical or different heteroatom and/or heterogroups. Heteroatoms and preferably oxygen, sulphur or nitrogen and heterogroups are N-alkyl, the alkyl or N-alkyl group preferably containing 1 to 4, in particular 1 or 2, carbon atoms. Alkyl which may be mentioned is methyl, ethyl, n- and i-propyl and n-, i- and t-butyl. The heterocyclic ring contains 5 to 7, preferably 5 or 6, ring members.

Examples of the heterocyclic ring which may be mentioned are pyrrolidine, piperidine, piperazine, hexamethylenimine, morpholine and N-methylpiperazine.

Very particularly preferred compounds which may be mentioned are compounds of the general formulae (II) and (III):



(II),



(III),

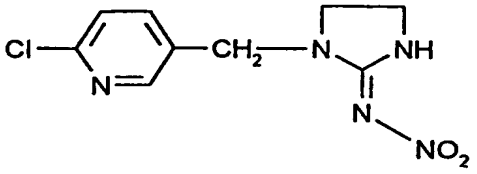
in which

n represents 1 or 2,

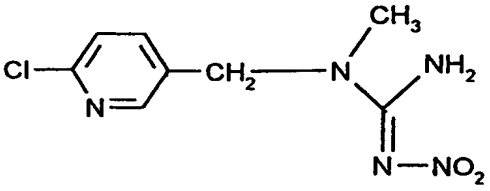
Subst. represents one of the abovementioned substituents, in particular halogen, very particularly chlorine,

A, Z, X and E have the meanings given above.

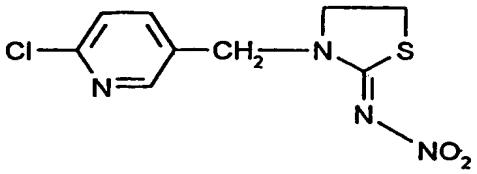
The following compounds may be mentioned specifically:



(IVa)



(IVb)



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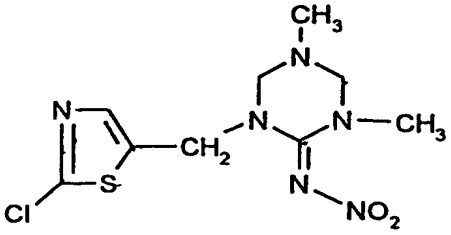

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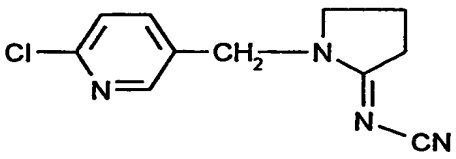

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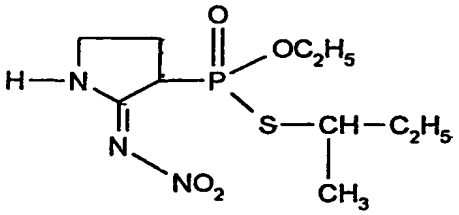
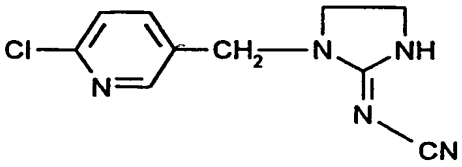
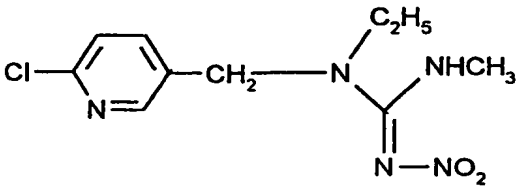


(IVf)



(IVi)



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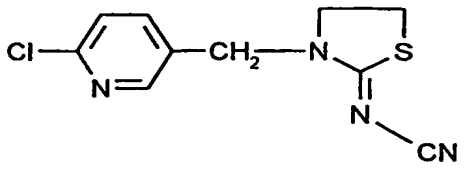

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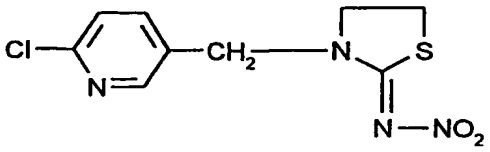

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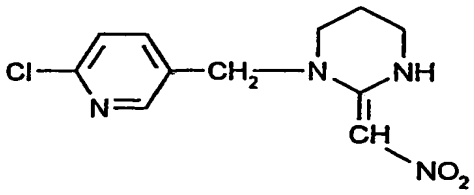

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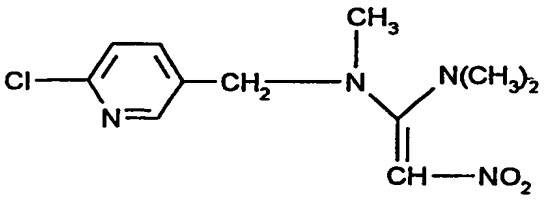

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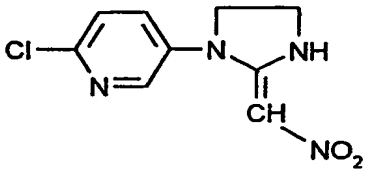

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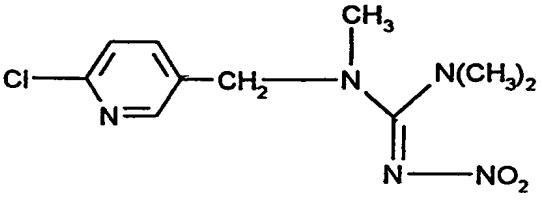

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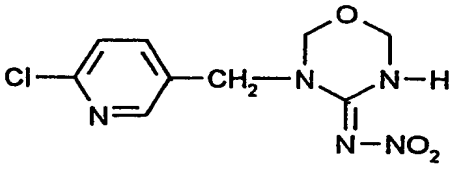

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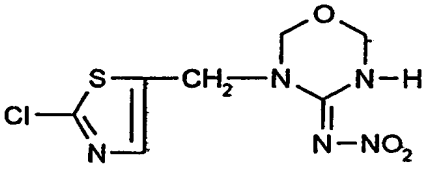

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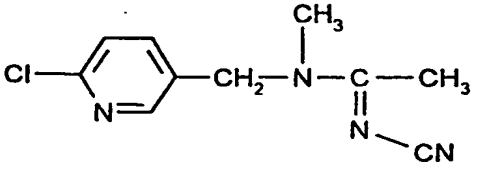

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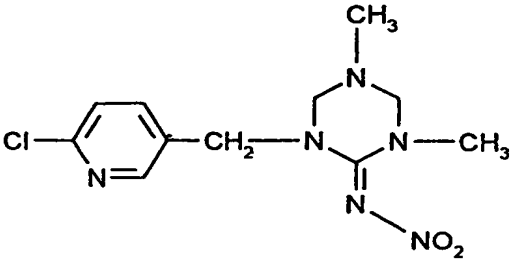

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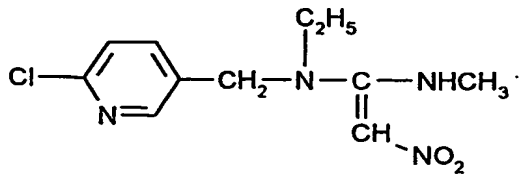
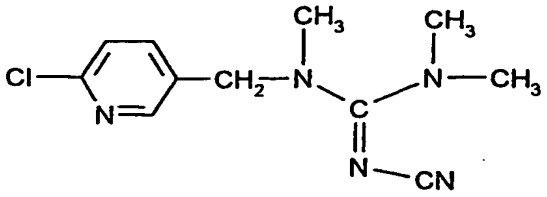


(IVu)



(IVv)

the compound of the formula (IVa), imidacloprid, being particularly preferred.

Glues and adhesives are regarded as binders which are employed for the manufacture of plywood sheets and timber material sheets.

In the manufacture of wood composites, typically the following bonding agents are used: glues based on urea/formaldehyde, urea/melamine, isocyanates such as MDI, phenol/formaldehyde, phenol/resorcinol/formaldehyde, or urea/resorcinol/formaldehyde. Normally, the bonding agents are prepared by mixing the glues with water, curing agents, and if desired with water repellents, biocides, extenders and/or buffering agents prior to the application to the wood particles, flakes or veneers. In addition to the active compounds of the formula (II), further biocides, such as, for example, other insecticides, and in particular fungicides having an action against Basidiomycetes and moulds, can be incorporated into the bonding agent.

Timber material sheets in this case are artificial wood sheets, such as, for example, plywood sheets, chipboards and fibreboards, which in general are manufactured from cut pieces of wood and a binder under pressure and with heat treatment.

The active compounds are mixed with these binders such that either finished formulations are obtained which can be employed directly in the sheet manufacturing process, or the active compounds are added during or shortly before sheet manufacture. The amount of active compound and binder is calculated from the volume of the manufactured sheets according to generally known methods.

The active compounds can be incorporated into a wood composite through a number of routes, for example:

1. Treatment of the flakes/wood particles, before or after drying, using an additional sprayhead or blender system.

2. Mixing the chemical with the adhesive and/or wax which is subsequently applied to the flakes in the blender.

3. Spraying the flakes with a preservative solution or emulsion, or mixing the powdered chemical with the flakes in the blender.

4. Metering a powdered preservative onto the dried flakes immediately before the blender. The powder is then mixed with the flakes in the blender

Adding the chemical as a mixture with the adhesive or wax is probably the most convenient from the manufacturer's viewpoint. However, mixing the active compounds with the adhesive can cause biocide efficacy problems, especially, when the biocide is decomposed in the adhesive by hydrolyzation or other chemical reactions. Incorporation with the wax is safer, but often the wax distribution is not as good as that of the adhesive. This in turn may also influence the effectiveness of the biocide.

The active compounds can either be added as they are to the glue or in a preformulated form, for example prediluted in solvents, e.g. glycols, glycol ethers, aliphatic and/or aromatic hydrocarbons, esters, alcohols or ketones, or emulsified or dispersed in water. Alternatively, the active compounds or formulations thereof can be applied to the wood particles, flakes or veneers separately from the glue either to the wood particles before blending with the glue or after blending with the glue or even after the gluing process, i.e. to the finished wood composite.

The invention furthermore also relates to incorporating, additionally to the active compounds of the formula (II) and the binder, still further active compounds such as,

for example, other insecticides, but in particular fungicides having action against Basidiomycetes, into the plywood and timber material sheets.

Preferred fungicides are IF-1000, IPBC and azoles such as tebuconazole, propiconazole and cyproconazole. In combination with the active compounds of the formulae IIa) to IIi), these mixtures have particularly good activities and stabilities.

The following examples substantiate the invention without limiting it to these examples.

The results show experiments against termites, chipboard being employed which are manufactured using a formulation of a strongly alkaline phenolic resin containing the compound of the formula (IVa).

Type of wood for plywood	Radiata pine
Layer structure	1.5 mm + 3.0 mm + 1.5 mm (3 layers)
Dosage	a) 1.5 kg/m^3
	b) 2.0 kg/m^3
	c) 2.5 kg/m^3
Binder	a) Phenol resin adhesive A
	b) Phenol resin adhesive B
Manufacturing process	Quantity of paste 40 g/900 cm^2
	125°C, 10 kg/cm^2, 6 minutes

Example 1

Dose rate	Blank	1.5 kg (30 g ai)/m^3	2.0 kg kg (40 g ai)/m^3	2.5 kg (50 g ai)/m^3
Phenol resin A	250.0 g	250.0 g	250.0 g	250.0 g
Flour	4.2 g	4.2 g	4.2 g	4.2 g
Walnut powder	20.8 g	20.8 g	20.8 g	20.8 g
Sodium	3.3 g	3.3 g	3.3 g	3.3 g

carbonate				
Curing agent	5.8 g	5.8 g	5.8 g	5.8 g
Wood preservative	-	6.3 g	8.5 g	10.7 g

Example 2

Dose rate	Blank	1.5 kg (30 g ai)/m^3	2.0 kg (40 g ai)/m^3	2.5 kg (50 g ai)/m^3
Phenol resin B	250.0 g	250.0 g	250.0 g	250.0 g
Flour	30.0 g	30.0 g	30.0 g	30.0 g
Sodium carbonate	20.0 g	20.0 g	20.0 g	20.0 g
Curing agent	5.0 g	5.0 g	5.0 g	5.0 g
Wood preservative	-	6.3 g	8.5 g	10.7 g

Assessment

The test is carried out in accordance with JWPA Standard No. 11. 150 termite workers and 15 termite soldiers were put for 21 days into a container which contains a test piece of chipboard.

Example 3 (Phenol resin A)

Dose rate	% weight loss	% mortality
Blank	14.20	16.0
1.5 kg (30 g ai)/m^3	2.50	57.5
2.0 kg (40 g ai)/m^3	1.35	100.0
2.5 kg (50 g ai)/m^3	1.50	100.0

Example 4 (Phenol resin B)

Dose rate	% weight loss	% mortality
Blank	21.90	20.0
1.5 kg (30 g ai)/m^3	0.55	49.0
2.0 kg (40 g ai)/m^3	0.00	100.0
2.5 kg (50 g ai)/m^3	0.00	100.0

Example 5

Various sheets consisting of chips are manufactured:

Type of wood: Albizzia (broad leaf tree produced in Indonesia)

Chip size:

5-10 mesh	9 %
10-20 mesh	40 %
20-40 mesh	30 %
40-60 mesh	9 %
60-80 mesh	5 %
80 - mesh	6 %

Manufacturing process:

Sheet size 30 x 30 x 1 cm

Sheet thickness 0.7

Composition of the sheet

Chip	500 g
Urea resin	50 g
Curing agent	0.85 g
Wood preservative (see Table)	

Pressure conditions

30 kg/cm^2 for 5 minutes

10 kg/cm^2 for 5 minutes

Mechanical strength of the sheets

Dose rate	Blank	139 g/cm^3	208 g/m^3	833 g/m^3
Specific gravity	0.75	0.73	0.71	0.75
Peeling strength (kg/cm^2)	6.0	5.0	5.1	5.0
Flectural strength (kg/cm^2)	80.0	72.0	65.0	86.0

Anti-termite action

Chemical name & Dose rate		% weight loss	% mortality	
			Worker termite	Soldier termite
Blank		5.73	22.0	76.7
Chlorpyriphos	350 g/m^3	0.07	100.0	100.0
	520 g/m^3	0.17	100.0	100.0
	690 g/m^3	0.07	100.0	100.0
Imidacloprid	70 g/m^3	0.00	100.0	100.0
	104 g/m^3	0.00	100.0	100.0
	138 g/m^3	0.00	100.0	100.0
Imidacloprid + IPBC	70 g/m^3	0.00	100.0	100.0
	104 g/m^3	0.00	100.0	100.0
	138 g/m^3	0.00	100.0	100.0

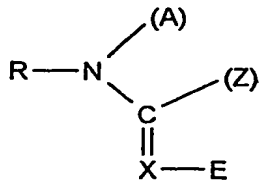
Viscosity of the mixture of resin and active compound

(cps)

	Temp.	Just after	1 day	5 days	10 days	15 days	20 days	25.days
Blank	5°C	11.0	11.1	11.5	12.0	12.4	13.2	13.5
	20°C	2.0	2.3	2.5	3.1	4.0	5.0	6.5
	30°C	1.1	1.4	2.2	4.8	12.3	N/T	N/T
Imid-	5°C	11.0	11.2	11.5	12.2	12.6	13.2	13.6
acloprid	20°C	2.2	2.3	2.5	2.9	4.0	5.3	6.4
(0.5 %)	30°C	1.1	1.6	2.5	4.7	12.5	N/T	N/T
Imid-	5°C	10.8	11.0	11.4	12.1	12.1	13.1	13.5
acloprid	20°C	2.2	2.3	2.6	3.0	4.2	5.0	6.7
(1.0 %)	30°C	1.0	1.0	2.3	5.0	12.3	N/T	N/T
Imid-	5°C	11.0	11.1	11.5	12.2	12.4	13.1	13.5
acloprid	20°C	2.2	2.4	2.7	3.2	4.1	5.2	6.5
(1.5 %)	30°C	1.1	1.4	2.3	4.8	12.4	N/T	N/T
Imid-	5°C	11.0	11.3	11.6	12.4	12.9	13.6	14.0
acloprid	20°C	2.2	2.3	2.6	3.2	4.0	4.9	6.6
(2.0 %)	30°C	1.1	1.4	2.5	4.8	12.7	N/T	N/T

Patent claims

1. Compositions containing at least one compound of the formula (I)



(I),

in which

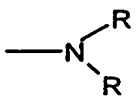
R represents hydrogen, optionally substituted radicals of the group consisting of acyl, alkyl, aryl, aralkyl, heteroaryl and heteroarylalkyl;

A represents a monofunctional group from the series hydrogen, acyl, alkyl, aryl, or represents a bifunctional group which is linked to the radical Z;

E represents an electron-withdrawing radical;

X represents a monofunctional group from the series alkyl, -O-R, -S-R,

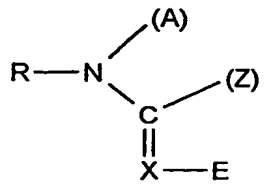
Z represents a monofunctional group from the series consisting of alkyl, -O-R, -S-R,



or represents a bifunctional group which is linked to the radical A or the radical X,

and binders or adhesives which can be employed for the manufacture of chipboards and timber material.

2. Use of compounds of the general formula (I)



(I),

in which

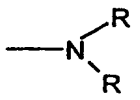
R represents hydrogen, optionally substituted radicals of the group consisting of acyl, alkyl, aryl, aralkyl, heteroaryl and heteroarylalkyl;

A represents a monofunctional group from the series hydrogen, acyl, alkyl, aryl, or represents a bifunctional group which is linked to the radical Z;

E represents an electron-withdrawing radical;;

X represents the radicals -CH= or =N-, it being possible for the radical -CH= to be linked to the radical Z instead of an H atom;

Z represents a monofunctional group from the series alkyl, -O-R, -S-R,



or represents a bifunctional group which is linked to the radical A or the radical A or the radical X,

for the manufacture of chipboards and timber materials..

3. Chipboards and timber materials comprising a compound of the formula (I) according to Claim 1.

INTERNATIONAL SEARCH REPORT

Interr.. .onal Application No
PCT 97/05776

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 A01N51/00 C09J201/00

According to International Patent Classification(IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 A01N C09J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 511 541 A (BAYER AGROCHEM KK) 4 November 1992 see claims see page 3, line 7 - line 10 see page 4, line 39 - line 41	1-3
X	WO 96 10915 A (BAYER AG ;UHR HERMANN (DE); KUGLER MARTIN (DE); SCHRAGE HEINRICH () 18 April 1996 see claims 1,3,5,6 see page 10, last paragraph see page 12, paragraph 2	1-3
A	DE 32 23 221 A (DESOWAG BAYER HOLZSCHUTZ GMBH) 22 December 1983 see page 6, paragraph 2	1-3

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
30 January 1998	17/02/1998

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Decorte, D

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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